

SPECTROSCOPIC STUDIES OF INTERSTELLAR GRAINS

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Prepared by  
F. M. Johnson

Approved by

*A. O. Jensen*

A. O. Jensen, Manager  
Electro-Optical Technology Laboratory



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## CONTENTS

1. INTRODUCTION	1
2. EXPERIMENTAL RESULTS	5
3. DISCUSSION	23
Scientific Report No. 1	
Scientific Report No. 2	

## ILLUSTRATIONS

1. Glass Dewar for Liquid Helium Transmission Measurements	6
2. Metal Dewar	7
3. Spectrum of Retinol at 77°K	9
4. Spectrum of Lycopene in EPA at Room Temperature	10
5. Spectrum of Lycopene in N-Octane at Room Temperature	11
6. Spectrum of Lycopene in EPA at 77°K	12
7. Spectrum of Carotene in EPA at Room Temperature	13
8. Spectrum of Carotene in EPA at 77°K	14
9. Spectrum of Carotene in EPA at 77°K, Thin Sample	15
10. Spectrum of Chlorophyll a at 4°K, Two Runs; Second Run was a Check Sample Evaporated on a Thin Glass Slide	16
11. Spectrum of Chlorophyll b at 4°K	17
12. Spectrum of Chlorophyll a in Pentene-2 at Room Temperature	18
13. Spectrum of Chlorophyll a in 3-Methylpentane at Room Temperature	19
14. Spectrum of Chlorophyll b in Pentene at Room Temperature	20
15. Spectrum of Chlorophyll b in 3-Methylpentane at Room Temperature	21
16. Major Interstellar Lines	24

## SECTION 1

### INTRODUCTION

This report comprises the first phase of a research effort directed towards an experimental and theoretical study pertaining to the chemical identification of the interstellar dust. The emphasis of this program has been primarily directed towards the spectral analysis of the interstellar diffuse bands and their correlation with laboratory observed absorption bands. Since none of the simpler diatomic, triatomic or molecules containing up to 12 atoms have been found to exhibit spectra even remotely resembling the interstellar line spectra, it was decided to examine the larger molecules, particularly the porphyrins.

Two scientific reports were prepared under the contract. The first one comprised an introduction to the subject and is entitled, "Interstellar Matter". The second report includes the results of the literature search as well as a summary of the theoretical analysis pertaining to the spectra of the porphyrins and related compounds. Preliminary experiments were undertaken during the course of this program. These are described in Section 2. Two dewars were procured for spectroscopic measurements at temperatures to as low as 4°K. One was a low-cost glass dewar with a permanently evacuated inner chamber enabling the use of liquid helium. The second dewar was all metal and required pump-out for each measurement. One of the main differences between the two dewars is the fact that the glass one requires the samples to be immersed in the refrigerant, whereas the all-metal dewar contains a cold finger which allows the cell to be in a vacuum environment, conditions more closely resembling those of interstellar space. A summary of the accomplishments during the program is as follows:

- a. Completed literature survey comprising over 1500 references delineating the most promising of the compounds and including references which may be pertinent to the subject (see Scientific Reports No. 1 and 2). The bibliography was further screened to include only those references which would be of interest to astronomers and exobiologists.
- b. Theoretical analysis and preliminary calculations were performed. These were of a preliminary nature only.
- c. In addition to the library search, information was gathered first hand from other scientists including astronomers, biologists, and chemists relating to information on the porphyrins and on the interstellar dust. This enabled the most recent astronomical data, for instance, to be included in our analysis. Dr. George Herbig of the University of California at Santa Cruz and Dr. C. R. O'Dell of the University of Chicago kindly supplied the author with important astronomical information. Thanks also go to Dr. G.A.H. Walker and Dr. B. Donn.
- d. Invited seminar talks were given on the subject of interstellar dust at the following institutions and dates:
  - (1) The Astronomical Society, Los Angeles, December 1966.
  - (2) Special Astronomy and Biodynamics Symposium convened at the University of California at Berkeley, January 20, 1967.
  - (3) Jet Propulsion Laboratory, February 24, 1967.
  - (4) California Institute of Technology, March 20, 1967.
  - (5) The Astronautical Society, Boston, May 26, 1967.

Important contact was made with scientists in the chemistry and exobiology fields. These included Professor Wolf Vishniac of the University of Rochester, Professor Henry Linschitz, Brandeis University, and Professor Harold C. Urey, University of California at San Diego. Also, very fruitful discussions were held with Professor Lloyd Motz of Columbia University. (A joint paper is in preparation.)

Although Report No. 1 outlines various models proposed by other scientists for the interstellar dust grains, it is worthwhile to point out here that the point of departure taken in our investigation was the assumption that the interstellar dust grains are comprised of cyclic hydrocarbons, i.e., porphyrin or similar compounds, for four basic reasons:

- a. The strongest interstellar absorption band at  $4430\text{\AA}$  would comprise the Soret band.
- b. The porphyrins are basically stable compounds.
- c. Porphyrins are stable against uv radiation.
- d. Roughly ten lines comprising these compounds are suggested by the interstellar bands. The claim is not made that unambiguous assignments can be made at this time. Far from it; a great deal more experimental work, particularly at low temperatures, is necessary in order to refine the measurements, particularly with respect to linewidth. No apologies need be made for considering these compounds, since the closest rival hypothesis considers graphite as the interstellar dust grain where there are absolutely no lines even remotely resembling the diffuse interstellar bands.

Moreover, homogeneous compounds such as graphite presuppose an orderly array of atoms laid down in the presence of an atmosphere of hydrogen atoms, the most abundant of elements. For more detailed discussions on other models, see Technical Report No. 1.



## SECTION 2

### EXPERIMENTAL RESULTS

Figures 1 and 2 are photographs of the glass and metal dewars, respectively. All the data discussed in this report were taken with the glass dewar. The metal dewar requires a vacuum station and associated equipment to be assembled in Phase II, Task A of the follow-on program. Some comments on the materials used are as follows:

It is extremely difficult to purchase the required porphyrins for study. Consequently, the data that was obtained does not represent the most promising of the porphyrin materials but only those compounds which can readily be purchased from suppliers such as Sigma Chemical Co. Chlorophyll a and b were examined a great deal; however, the more promising chlorophyll c could not be purchased. Table I (from Falk) gives, for chlorophyll c, absorption wavelengths at around 4430Å, 5800Å, and 6280Å in intensity ratios very closely resembling those of the diffuse interstellar lines.

It is planned to utilize the services of a chemist and/or biochemist in the Task B of the follow-on program to synthesize or extract chlorophyll c and other porphyrin type compounds which are not commercially available.

Meanwhile, our experimental program concentrated on the following aspects utilizing the materials at hand.

- a. The effect of solvents on the absorption band.
- b. The effects of temperature.
- c. The effects of changing the thickness of the sample in order to operate at a temperature of 4°K with reasonable sample transmission. No known substance, other than helium, remains a liquid at 4°K; consequently, it was thought that a very thin sample might be used. This indeed proved to be correct.

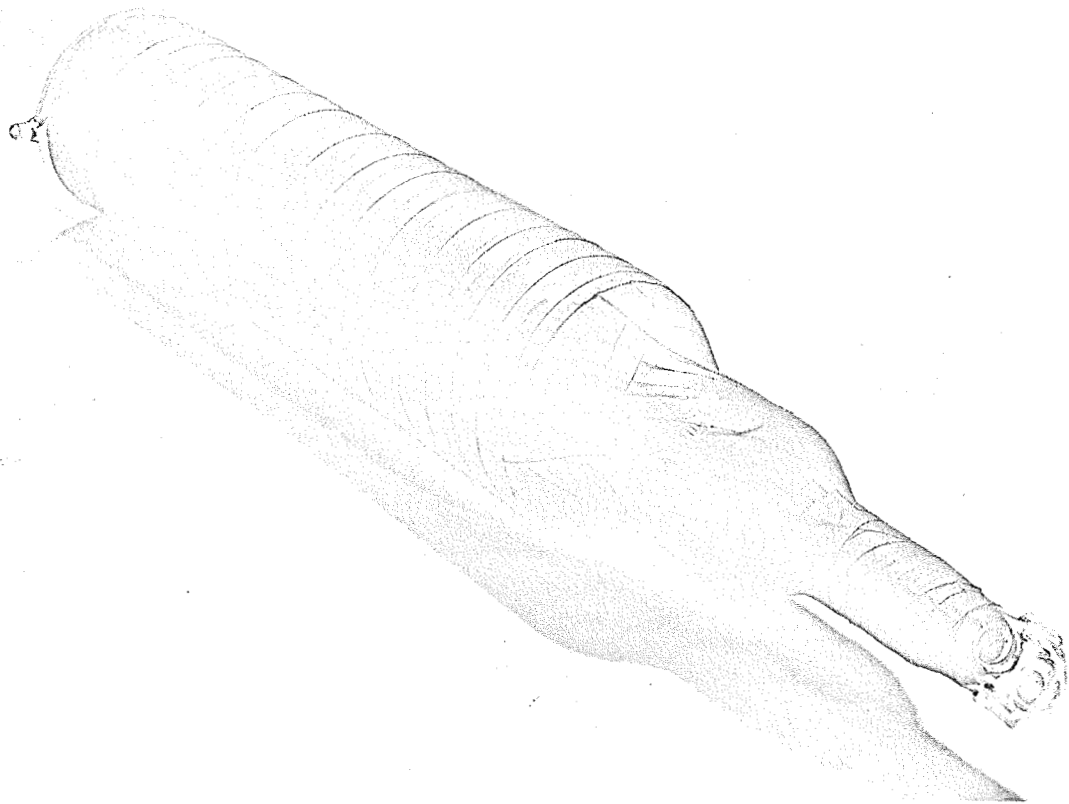


Figure 1. Glass Dewar for Liquid Helium Transmission Measurements

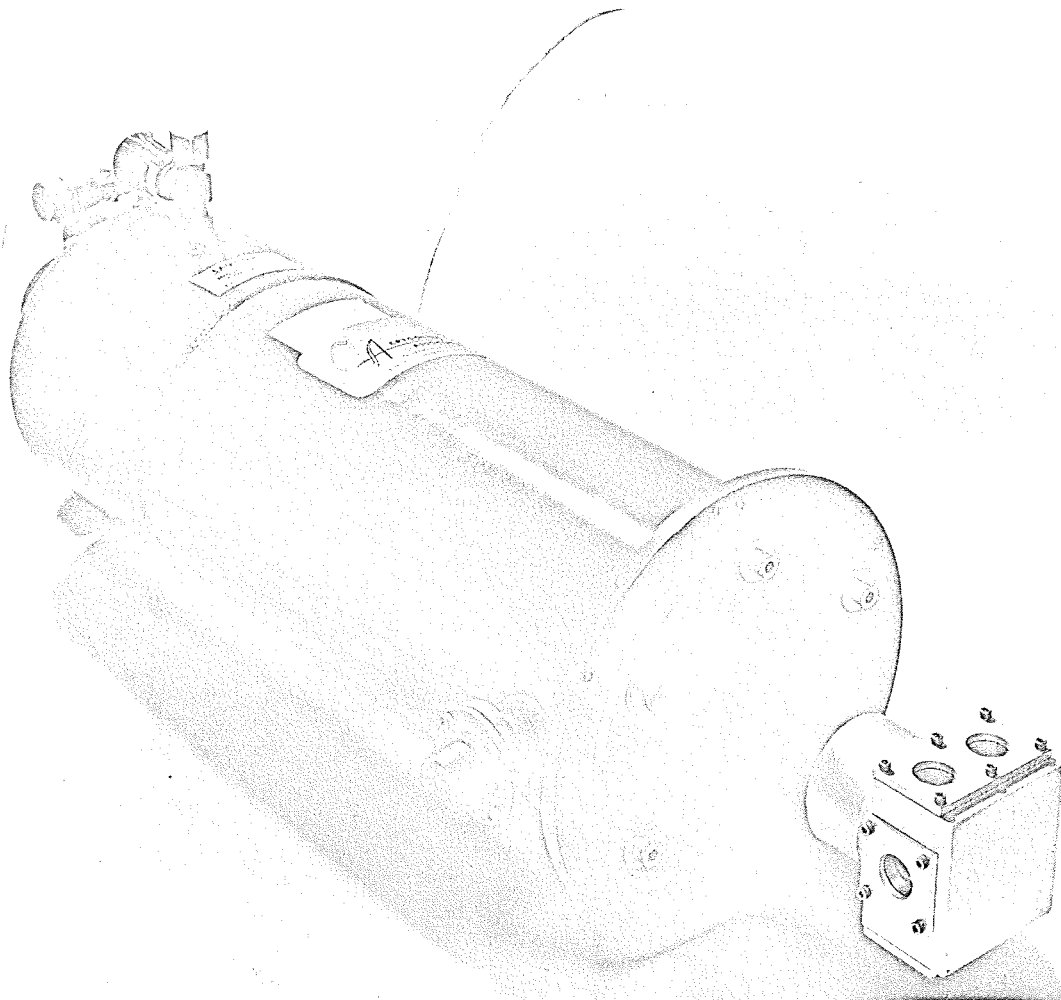


Figure 2. Metal Dewar. Photograph shows transmission windows.  
Cold-finger is situated within lower extension.

Another experimental approach was explored at great lengths, namely the duplication of the Sh'lovsky technique which utilizes specific hydrocarbons as solvents in order to sharpen up the absorption lines. Following the recipe given in the literature, it was not possible to duplicate the line narrowing, nor was it expected for chlorophyll. Data on carotene, a nonporphyrin, is included since this compound is usually associated with chlorophyll and furthermore does have absorption bands close to 4430 and 4700 at room temperatures. However, on cooling the sample to 77°K the intensity ratios did not seem favorable for the interstellar absorption identification. Moreover, no absorption lines are present beyond 5000Å. Retinol was explored at 77°K. The result shown in Fig. 3 is interesting since it shows a break in the scattering curve at around 4400. A similar break occurs in the interstellar light scattering data. Lycopene and carotene were also explored at room temperature and at 77°K and in various samples. The data is shown in Figs. 4 to 9. Finally, data of chlorophyll a and b taken at 4°K are shown (Figs. 10 and 11). The noise superimposed upon the data is presumably due to the rapid bubbling of the liquid helium in the chamber. The glass dewar allowed the retention of liquid helium for roughly half an hour only. The effect of solvents on the absorption data for chlorophyll a and b is shown in Figs. 12 through 15. Pentane and methylpentane were the solvents used. The absorption wavelengths shifted by as much as 40Å in some cases.

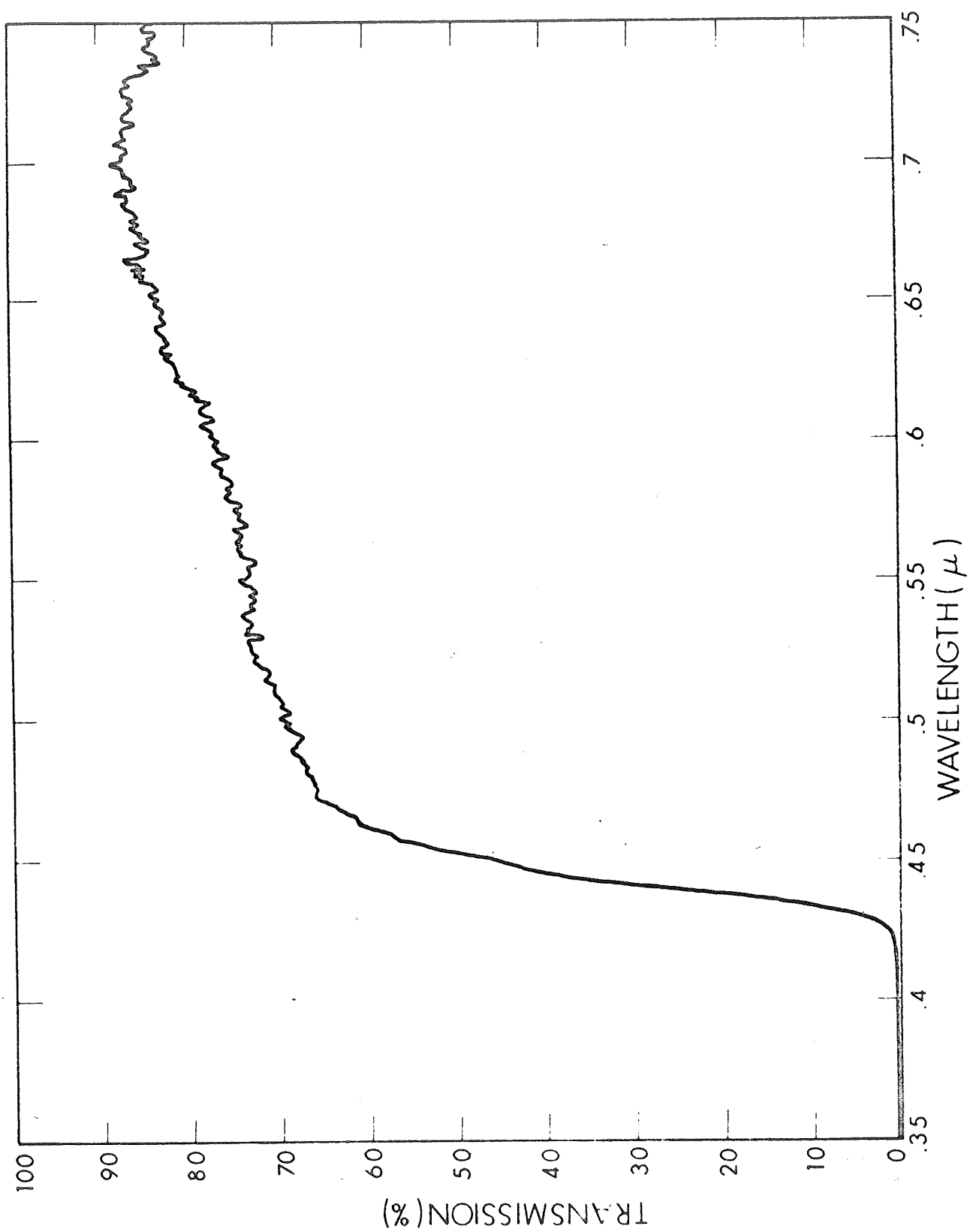


Figure 3. Spectrum of Retinol at 77°K

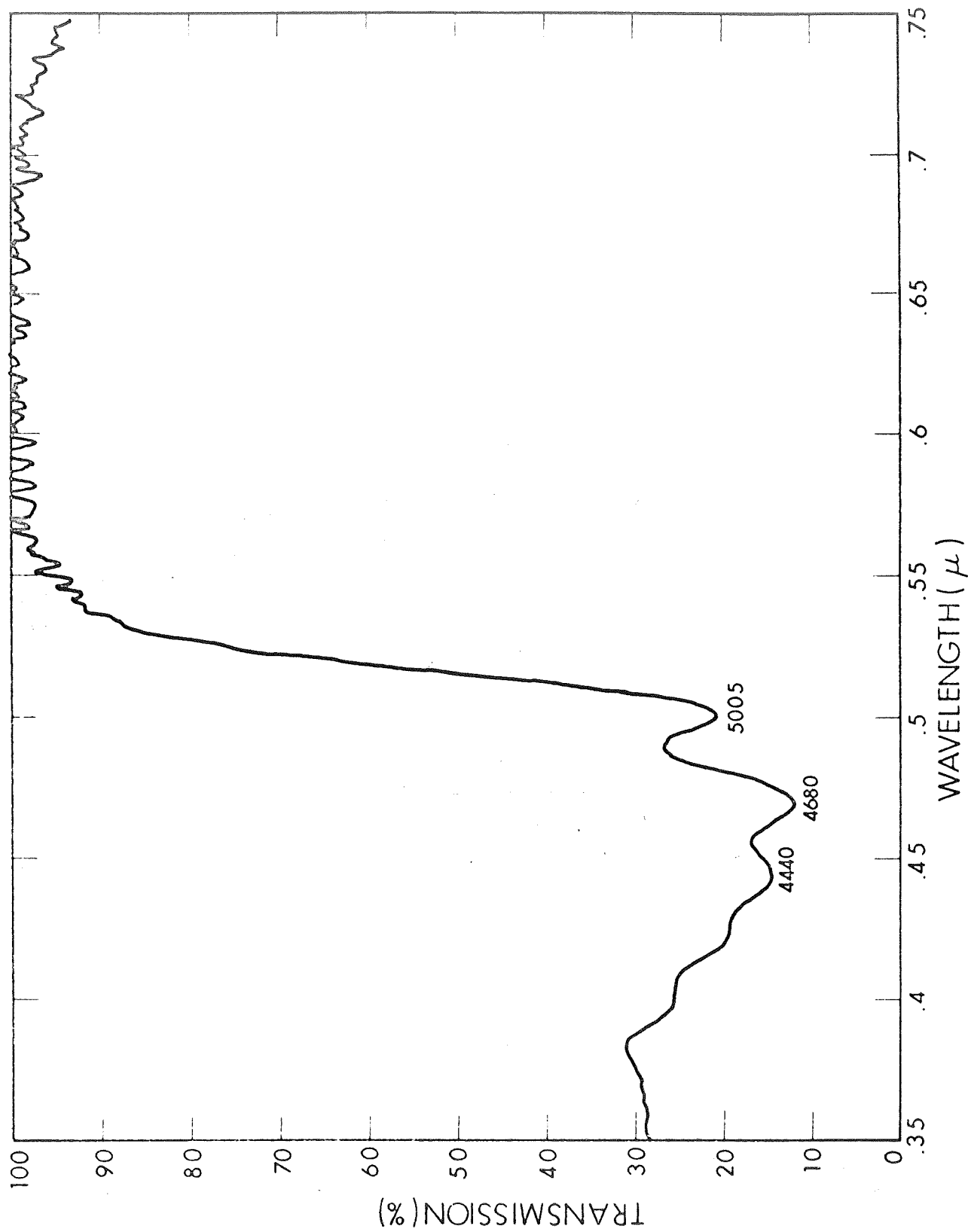


Figure 4. Spectrum of Lycopene in EPA at Room Temperature

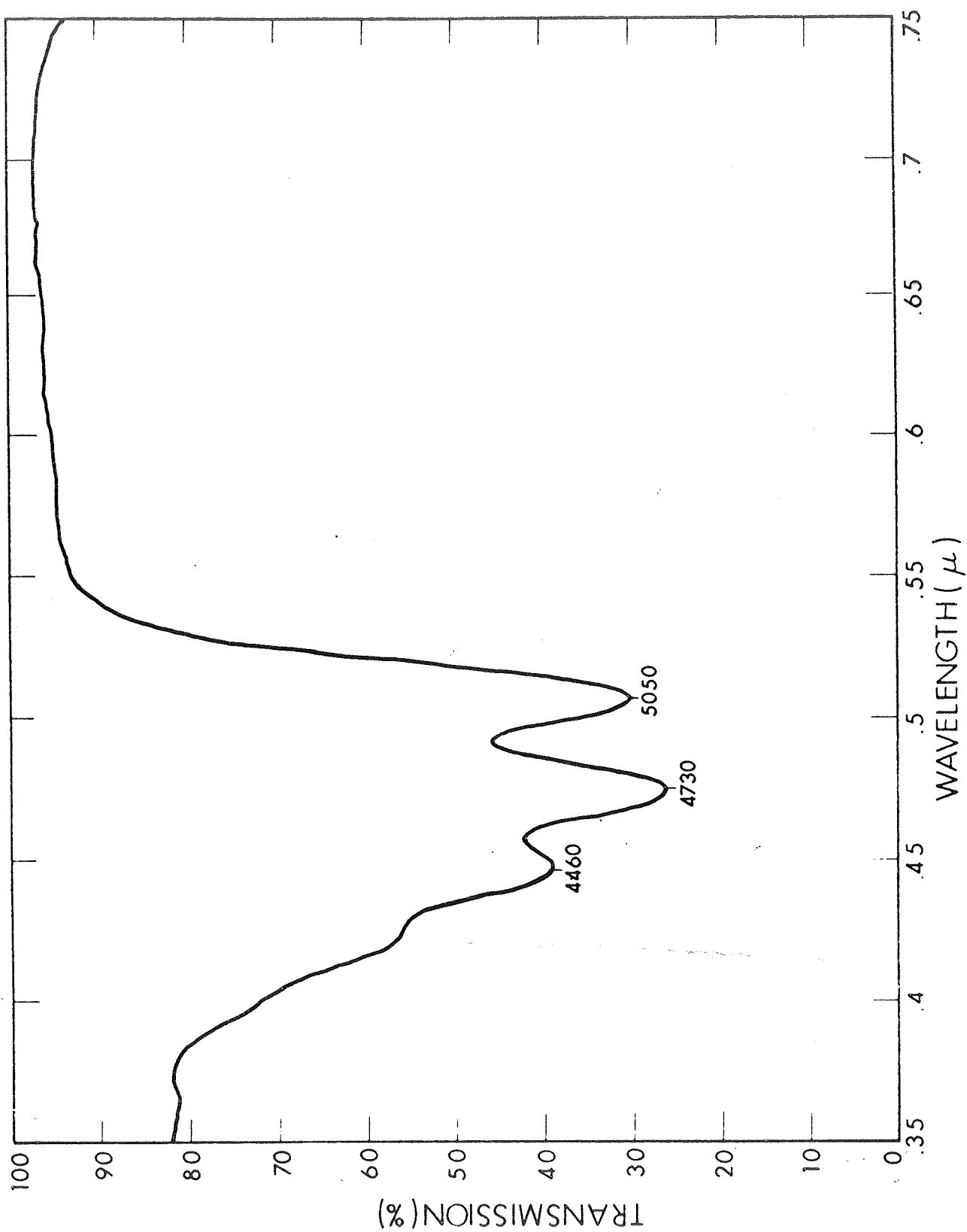


Figure 5. Spectrum of Lycopene in N-Octane at Room Temperature

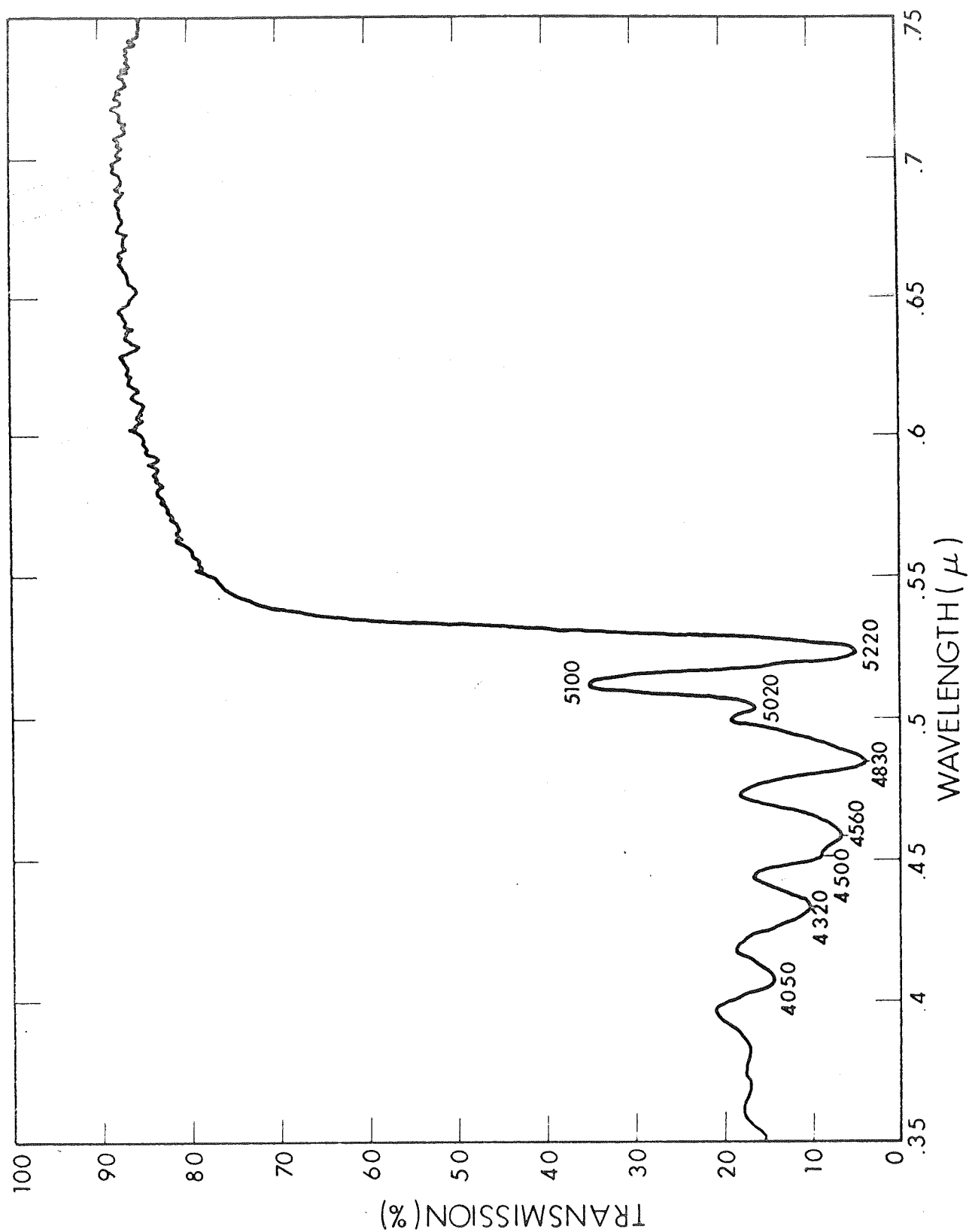


Figure 6. Spectrum of Lycopene in EPA at 77°K

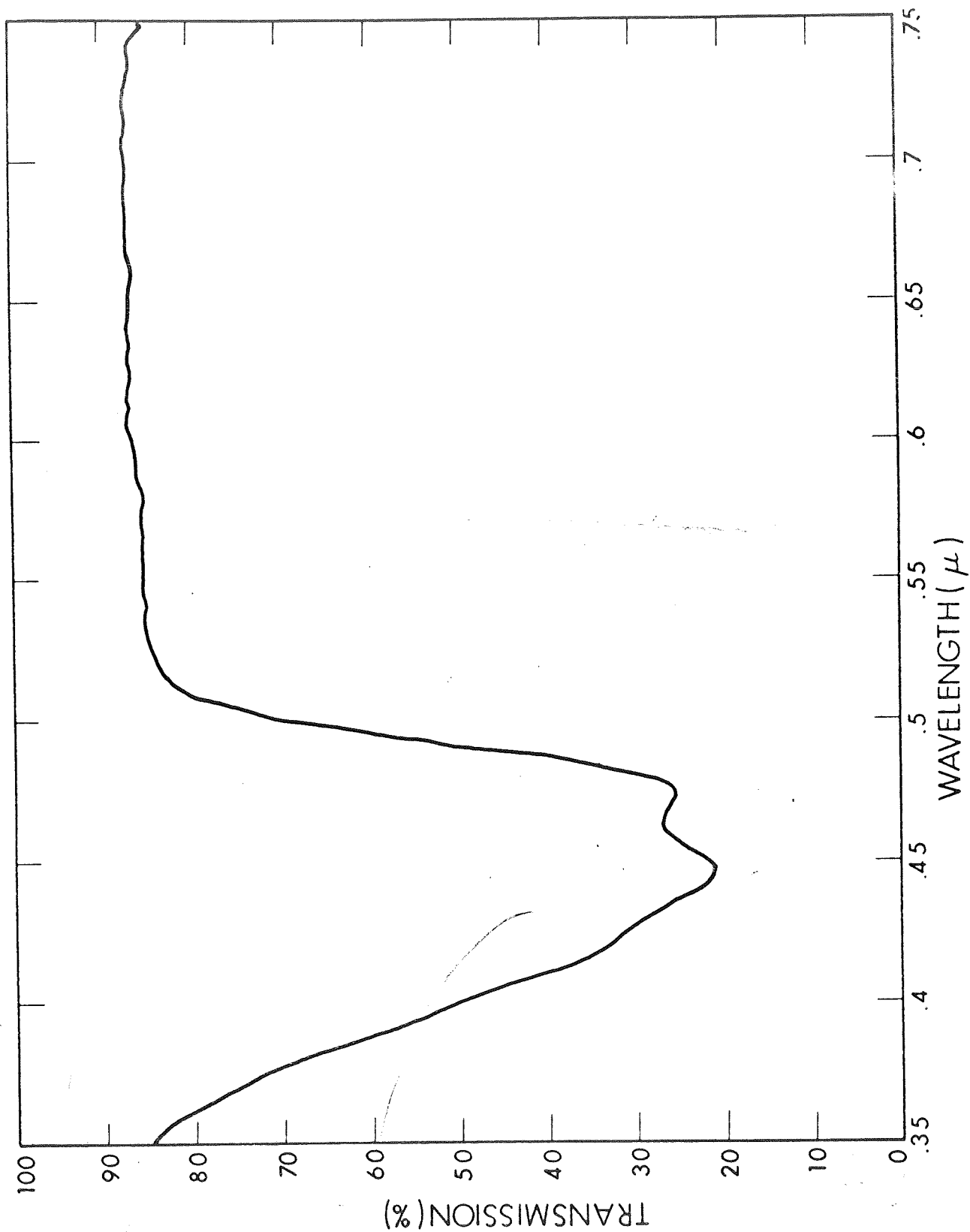


Figure 7. Spectrum of Carotene in EPA at Room Temperature

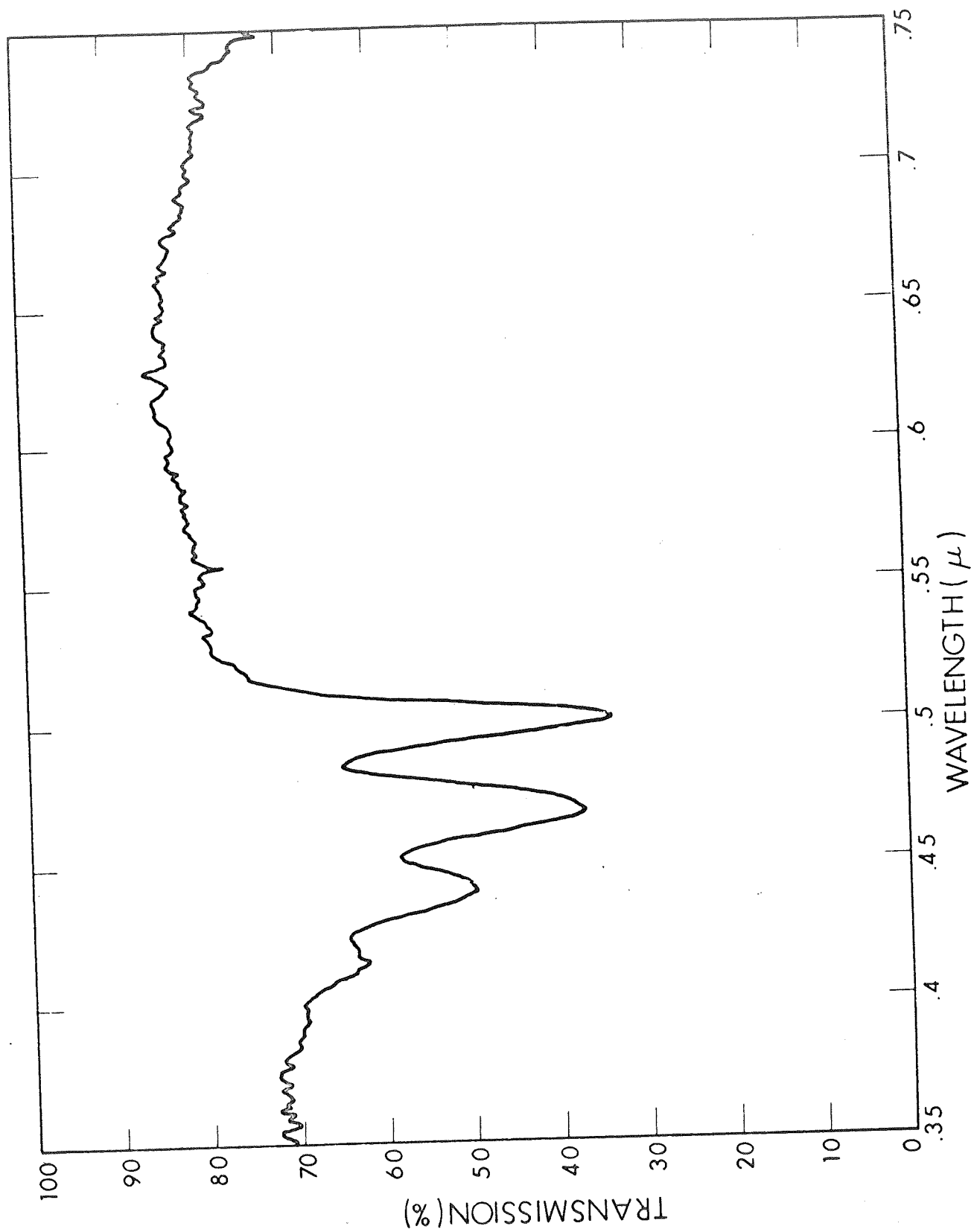


Figure 8. Spectrum of Carotene in EPA at 77°K

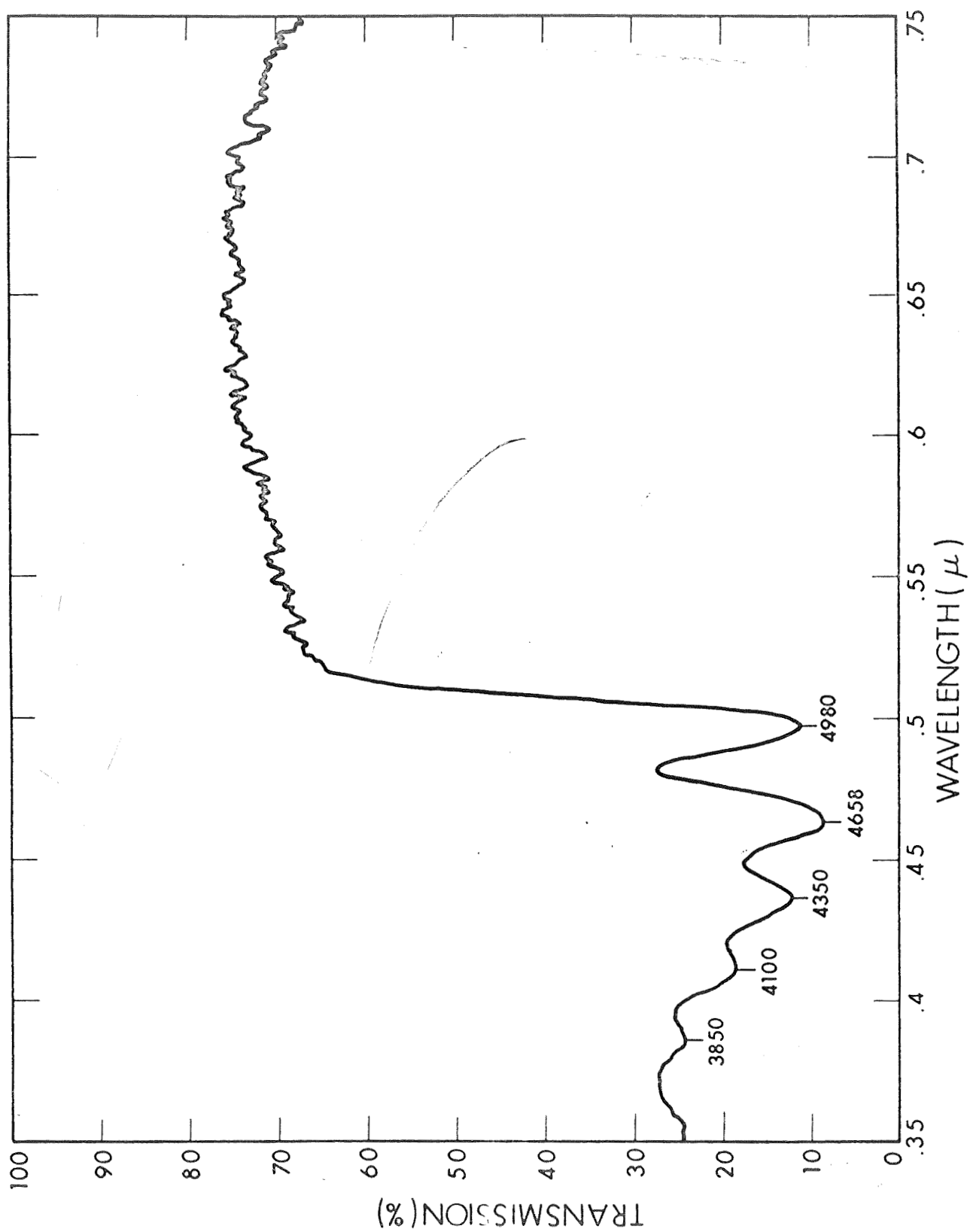


Figure 9. Spectrum of Carotene in EPA at 77°K, Thin Sample

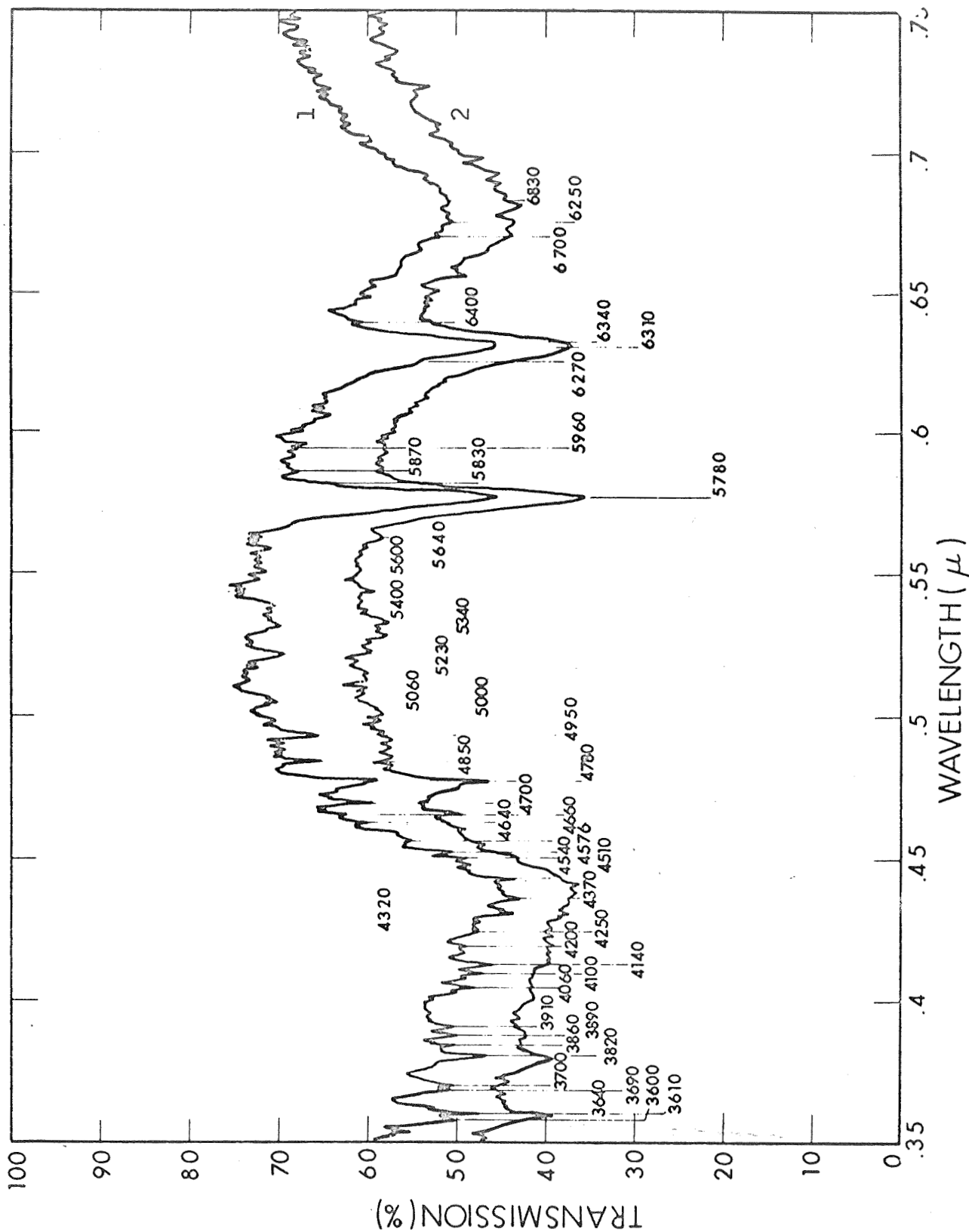


Figure 10. Spectrum of Chlorophyll a at 4°K, Two Runs; Second Run was a Check Sample Evaporated on a Thin Glass Slide

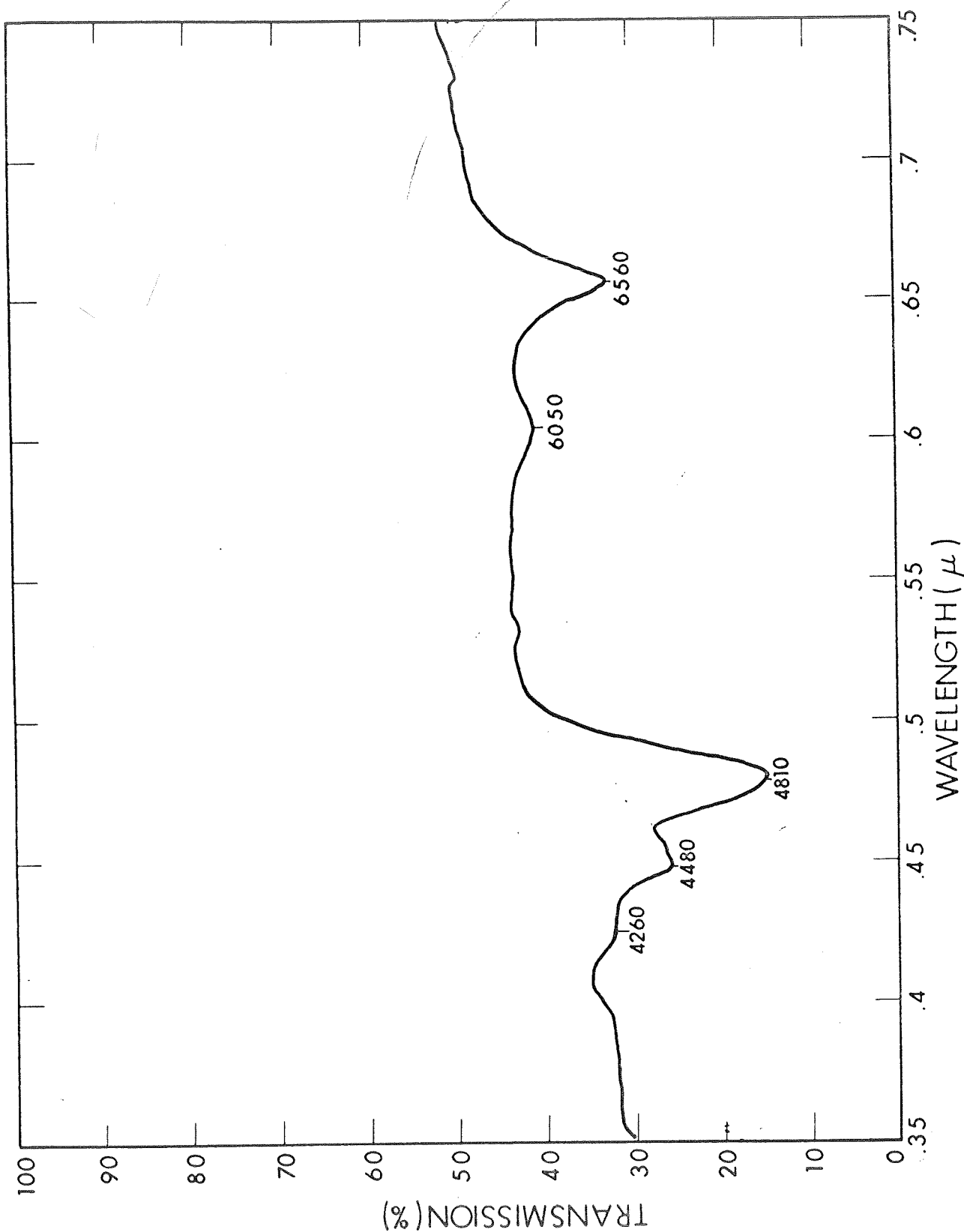


Figure 11. Spectrum of Chlorophyll b at 4°K

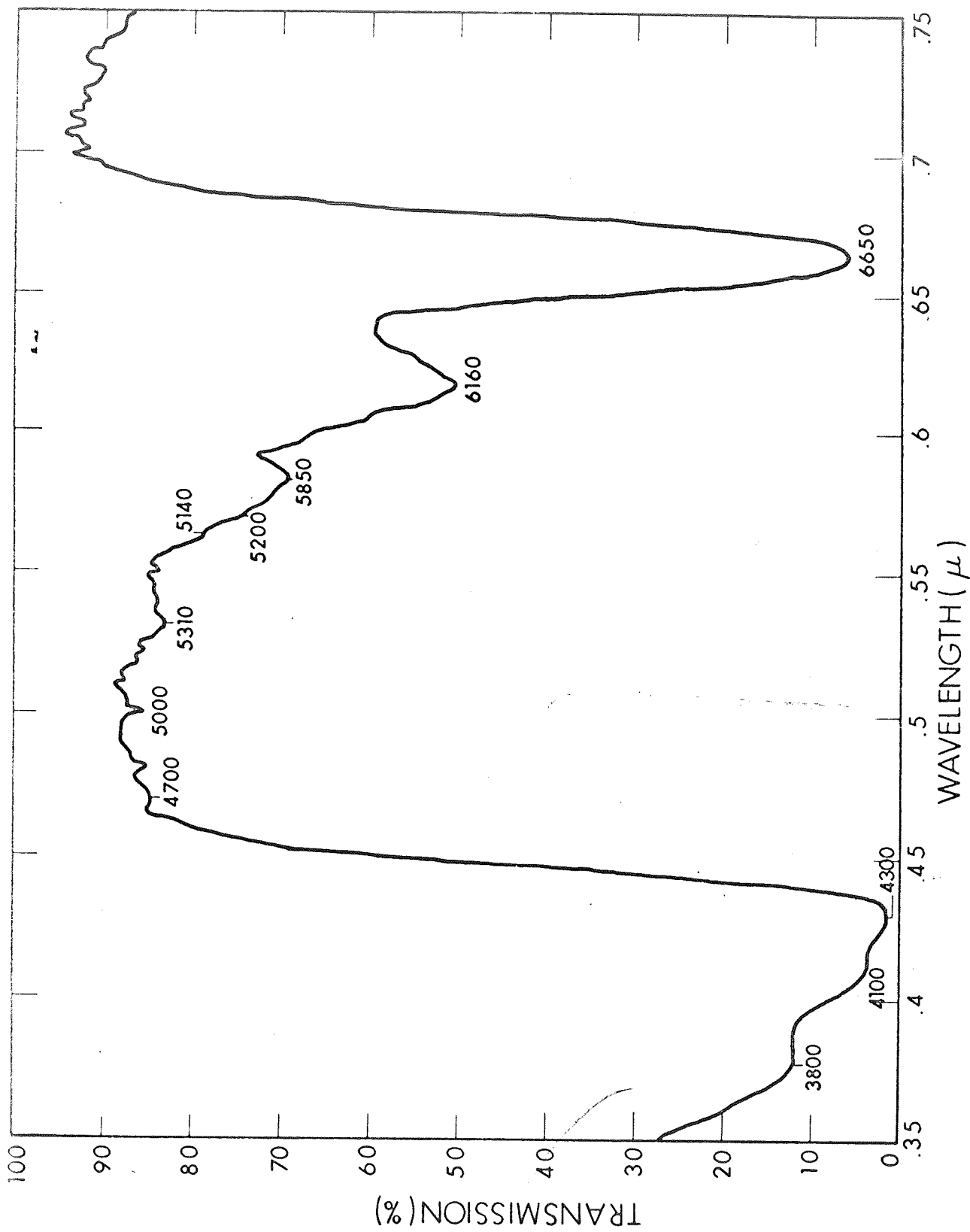


Figure 12. Spectrum of Chlorophyll a in Pentene-2 at Room Temperature

TABLE 5  
SUGGESTIONS FOR IDENTIFICATION OF  
INTERSTELLAR LINES

<u>Author</u>	<u>Scheme</u>	<u>Reference</u>	<u>Remarks</u>
A. Unsöld	Absorption of metallic particles of size $\lambda$	Z. Astro. <u>56</u> , 221 (1963)	Theory cannot predict individual wavelengths of absorption lines
C. A. Whitney	Absorption of metallic particles of size $\lambda$	Exptl. Smithsonian Institute Report No. 163 (1964)	Some crude experiments to test theory
G. H. Herbig	Absorption bands arising from metastable ground state of $H_2$ molecule	Ap. J. <u>137</u> , 200 (1963)	Requires $H_2$ molecules in excited states; would account for 4430 band only.
G. Herzberg	Predissociated bands of tri-atomic or poly-atomic free radicals similar to HCO or transitions of $O^-$ , $C^-$ , $N^-$	Liege Mem. <u>14</u> , 291 (1955)	No coincidences with interstellar lines so far
		Publ. Roy. Obs. Edinburgh <u>4</u> , 67 (1964) J. Opt. Soc. Am. <u>55</u> , 229 (1965)	See remarks by R. Wilson (1964) and rebutted by Herzberg (1965)
A. McKellar	Absorption lines in solid $O_2$	A. J. <u>60</u> , 170 (1955)	Would require matrix shifts -- very suggestive for about three diffuse lines

TABLE 5 (continued)  
SUGGESTIONS FOR IDENTIFICATION OF  
INTERSTELLAR LINES (contd)

<u>Author</u>	<u>Scheme</u>	<u>Reference</u>	<u>Remarks</u>
J. R. Platt	Quantum effects in 10-100Å size molecular-type particles	Ap. J. <u>123</u> , 486 (1956)	Particle-size dependent absorption wavelengths
F. M. Johnson	F-centers in alkali hydrides	Columbia Univ. Radiation Lab Progress Report 1955	Experimental width of F-center lines too wide at 4°K
E. E. Ferguson and	Molecular Complex Charge Transfer	J. Chem. Phys. <u>40</u> , 3715 (1964)	No coincidence found so far
H. P. Broida	Bands Example	Ap. J. <u>141</u> , 807 (1964)	
P. Swings and M. Desirant		Ciel et Terre No. 5, p. 160 (1939)	General Discussion on Absorption in Spectra in Solids at Low Temperatures
P. Swings and Y. Öhman	Suggest molecular crystals and amorphous metals	The Observatory <u>62</u> , 150 (1939)	
F. M. Johnson	Hydrocarbons H-C-N Conjugated Compounds	IAU Colloquium on Interstellar Grains Aug. 24-26 1965, Troy, N.Y., Bull. Am. Phys. Soc. Series II, <u>11</u> , 24 (1966) Am. Astronomical Society Meeting L.A. Calif. Dec. 1966	Very suggestive for a number of compounds.

TABLE 6  
DIFFUSE INTERSTELLAR LINES

Difference cm <sup>-1</sup>	* Wavelength (Å)	Difference cm <sup>-1</sup>	* Breadth	* Relative Intensity
228	4430.6		4	7
	4760*		4	2-3
	4882*		5	2-3
	5705**		3	0.1
	5780.4		2	0.8
	5797.0		1-2	0.2
	5849.7**	456	1	0.05
232	6010**	458	3	0.05?
	6176*		5	1-2
	6196.0**		1	0.05
	6203.0	456	2	0.1-0.2
	6270.0		2	0.2
230	6284.0		2	2
	6376.3**		1	0.02
	6379.3**		1	0.05
	6613.7		1	0.5
	6661**		1	0.2

Breadth numbers indicate the following:

4 - extremely broad, shallow absorption

3 - broad, hazy line

2 - diffuse line

1 - not quite so sharp as interstellar atomic features

\*Discovered by R. Wilson, Ap.J. 128, 57, 1958, and confirmed here by Herbig.

\*\*New Line. (Herbig)

The author is greatly indebted to Dr. Herbig for supplying this table comprising columns 2, 4 and 5 prior to publication.

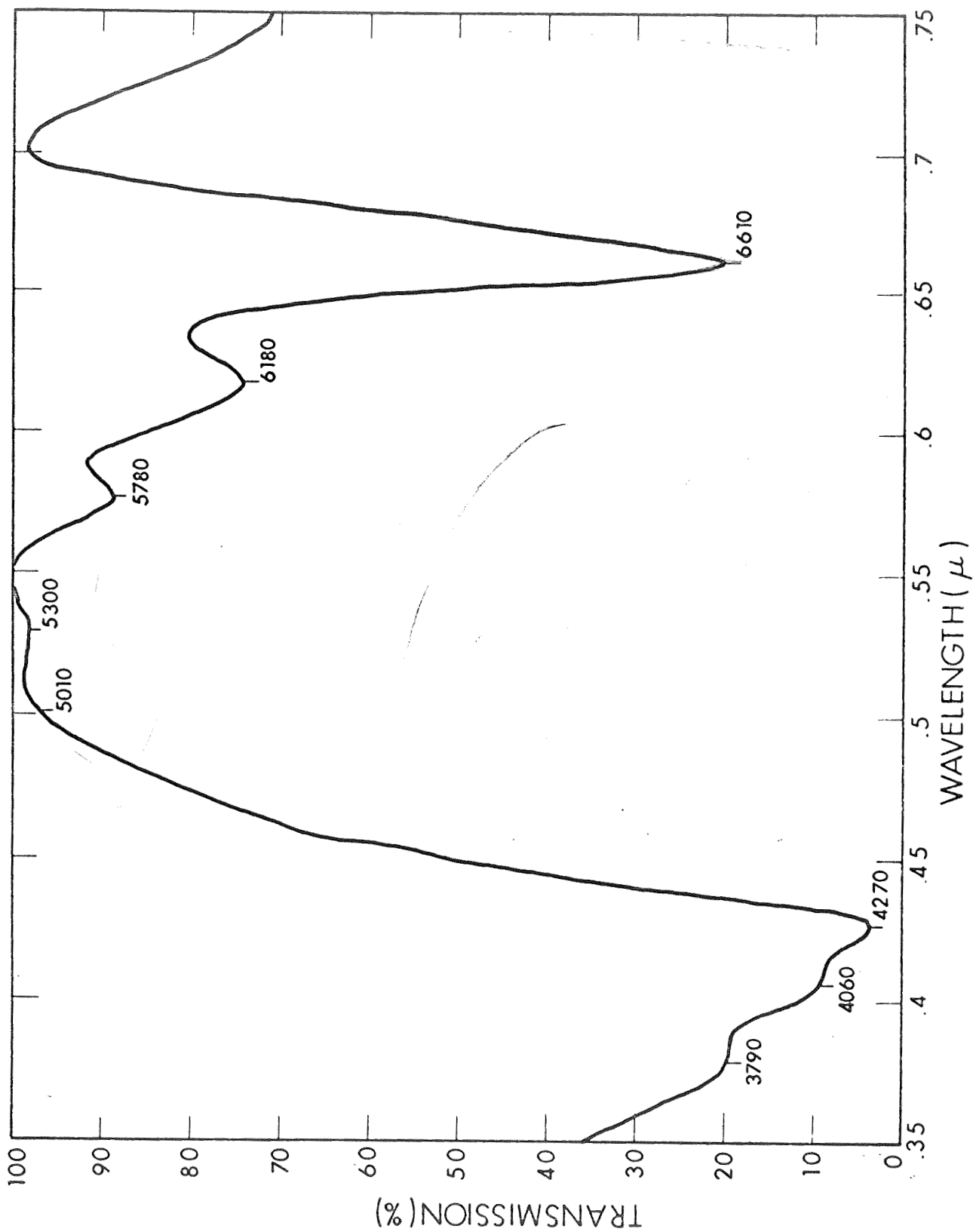


Figure 13. Spectrum of Chlorophyll a in 3-Methylpentane at Room Temperature

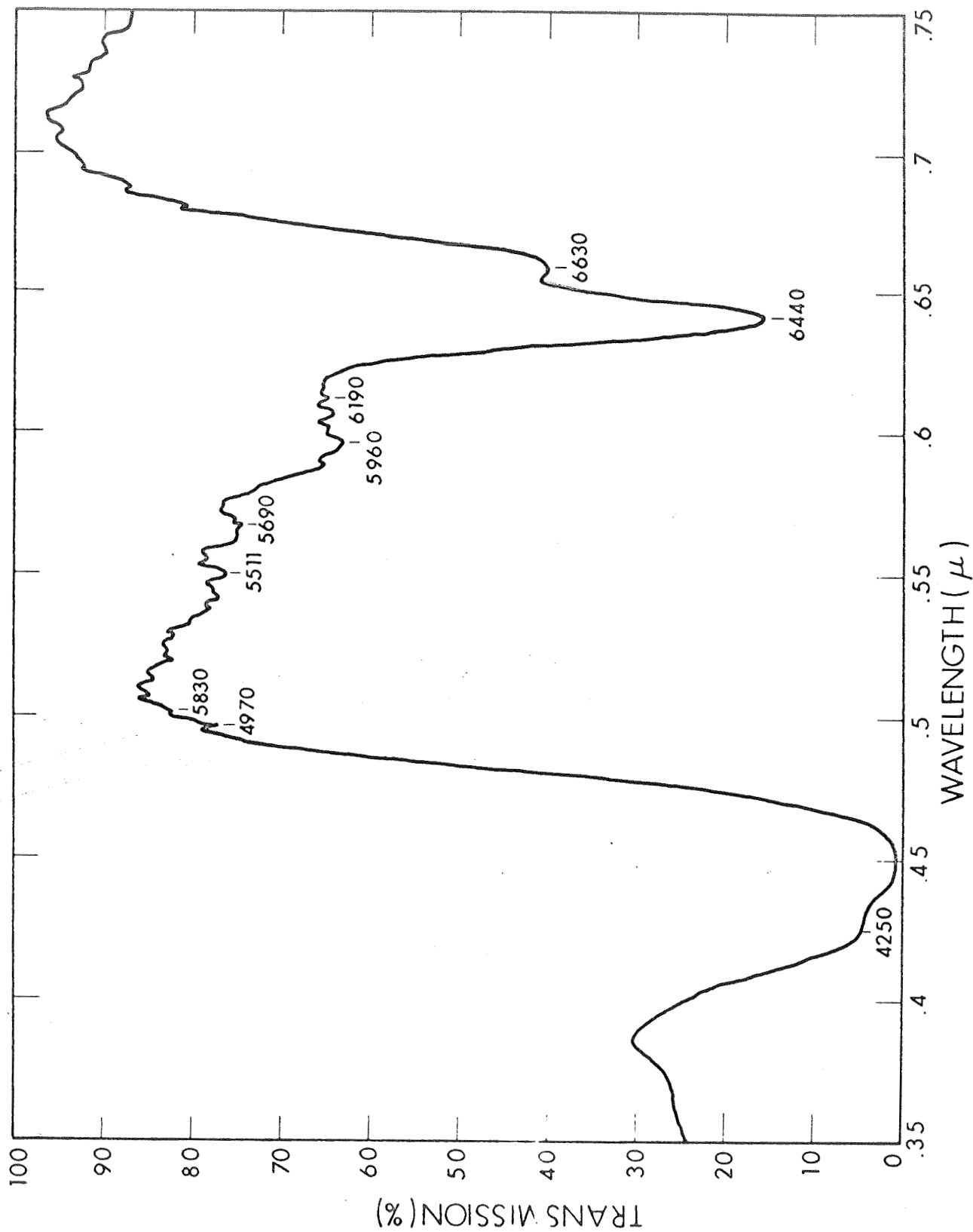


Figure 14. Spectrum of Chlorophyll b in Pentene at Room Temperature

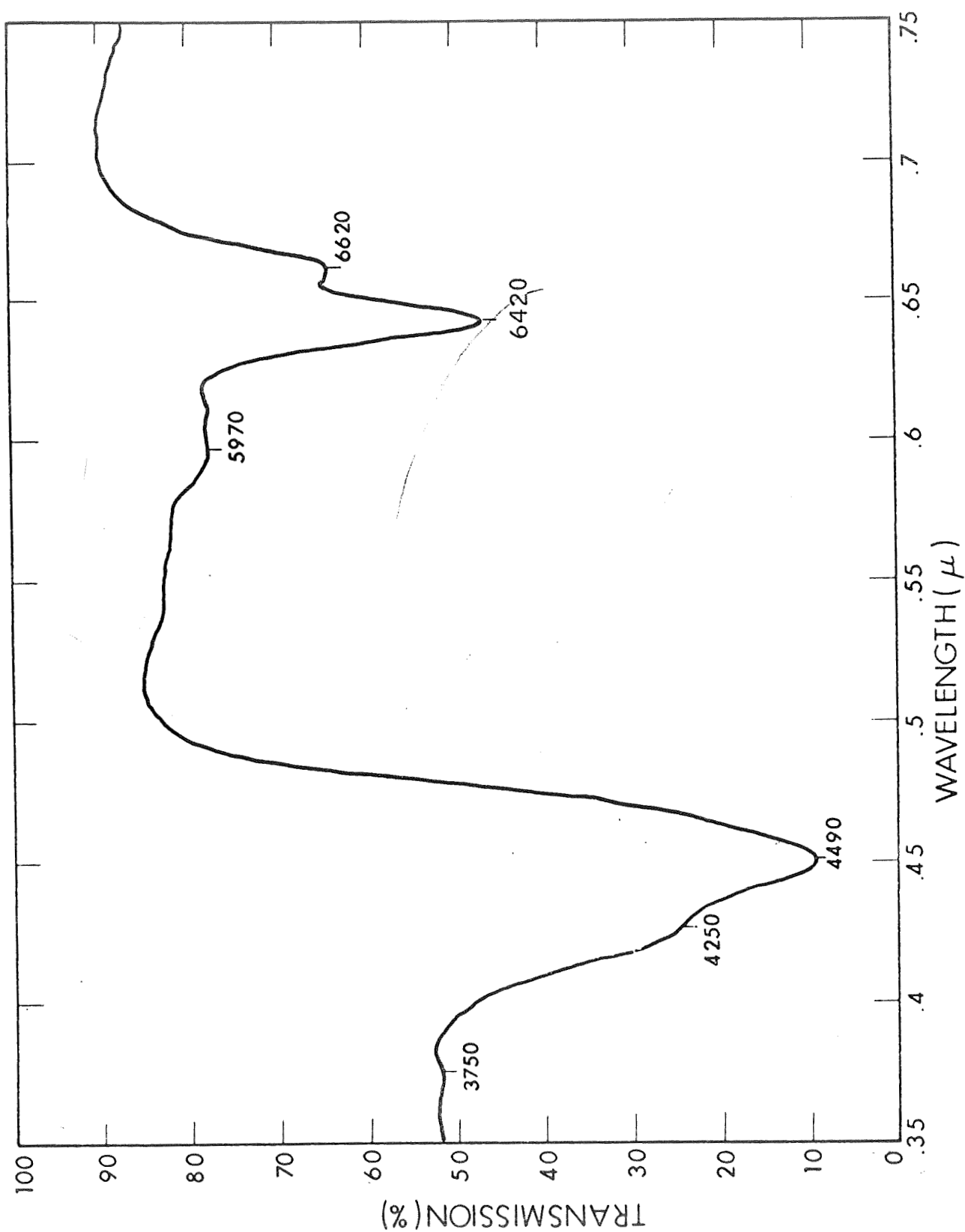


Figure 15. Spectrum of Chlorophyll b in 3-Methylpentane at Room Temperature



### SECTION 3

#### DISCUSSION

Figure 16 shows a major interstellar line including the very wide diffuse lines, the medium diffuse lines and experimental results indicated by arrows. The astronomical data includes unpublished results kindly supplied by Dr. George Herbig. The very wide lines at  $4000\text{\AA}$  still have to be verified. However, if correct, their presence would be extremely important since a large number of porphyrin compounds have the Soret peaks in that region. Only eight arrows are shown on the curve; a somewhat better case could be made by including more compounds. In any event, attention should be given to chlorophyll c which has not yet been examined at  $4^{\circ}\text{K}$ , and whose wavelengths are relatively close to those of the major interstellar diffuse bands as well as in the approximate intensity ratios. Further experimental absorption measurements are indicated, particularly with the haems. These experiments are planned in the follow-on program using the superior all-metal dewar and cold finger deposition technique.

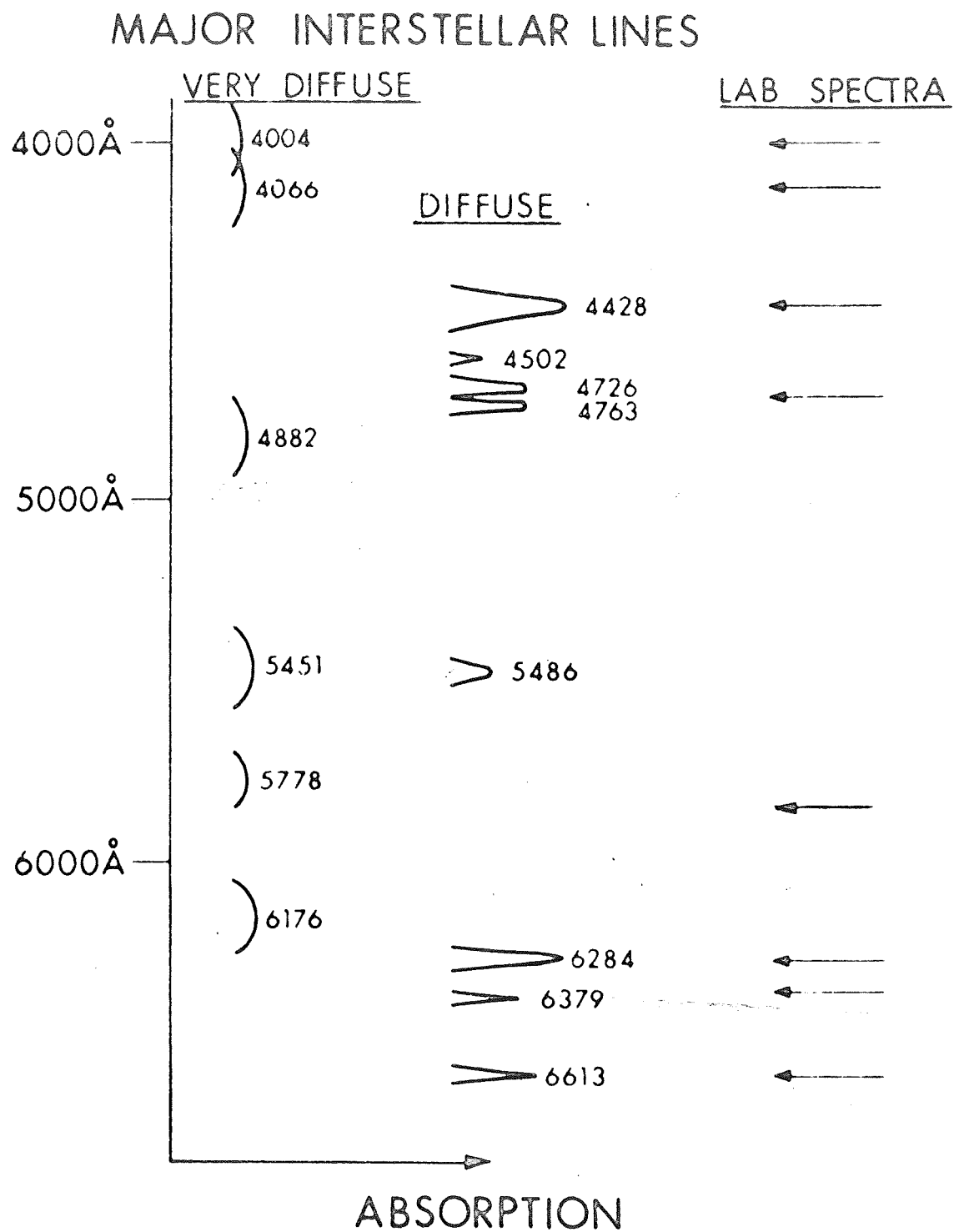


Figure 16. Major Interstellar Lines